COHESIVE ENERGIES AND OTHER PROPERTIES OF IONIC CRYSTALS—2. HALIDES OF COPPER, SILVER, THALLIUM AND AMMONIA

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ABSTRACT. Following the treatment employed in the case of alkali halides, the various crystal properties of other metal halides have been studied on the basis of a Lennard-Jones (12 : 6) potential energy form. Equations were modified to take into account the heavier metal halides such as of Copper, Silver, Thallium and Ammonia. The potential parameters were evaluated and the various properties computed. The agreement between the theoretical and experimental values served to justify the adequacy of the chosen potential form for these crystals also.

INTRODUCTION

Cohesive energies and few other properties of some of the simple alkali halide crystals, representing both the lighter and heavier compounds were computed using the Lennard-Jones (12 : 6) potential form in conjunction with the expression for the Coulomb energy (Sharma and Madan, 1964). As for the inert gases and nearly spherical molecules, different properties can be explained in terms of a simple potential such as one used, it was also found possible to describe the various properties of alkali halides adequately with its help. It was found that $n < 12$ is more suitable for lighter salts whereas $n = 12$ is appropriate for heavier ones. The inclusion of the van der Waals term makes the potential form more suitable for heavier compounds. In the present paper we consider properties of crystals heavier than alkali halides, that is, metal halides of Silver, Thallium, Copper and Ammonia and compare them with the experimental results. The characteristics of these salts show definite variation from alkali halides crystals and thus have to be treated separately.

COMPUTATION OF CRYSTAL PROPERTIES

Based on the Lennard-Jones (12: 6) potential form, the expression for the crystal energy can be written as

$$\phi(r) = \left(-\frac{\alpha e^2}{r} + \frac{B}{r^{12}} - \frac{C}{r^6} + \epsilon_0 \right) \qquad \ldots (1)$$

where α is the Madelung's constant, e is the electronic charge, ϵ_0 is the zero point energy, B and C are the repulsive and attractive parameters respectively and r is the interionic distance.

For alkali halide crystals, we had seen (Sharma and Madan, 1964) that the contribution of van der Waals energy term was small and therefore higher order terms such as dipole-quadrupole and others were not included in the expression for the crystal energy. However, van der Waals potentials show a systematic tendency to increase for salts of the heavier elements and as much the inclusion of the dipole-quadrupole term is important for these crystals. To consider the additional term (D/r^8), we replace C of equation (1) by C_1 where

$$C_1 = C\left(1 + \frac{D}{Cr^2}\right) \qquad \ldots (2)$$

The introduction of dipole-quadrupole term slightly changes the expressions for the repulsive force parameter B and the compressibility β, and therefore expressions for B and β can now be written as,

$$B = \frac{r^{12}}{12}\left(\frac{\alpha e^2}{r} + \frac{6C_2}{r^6} - \frac{3}{\beta}\right) \qquad \ldots (3)$$

where

$$C_2 = C\left(1 + \frac{8}{6}\frac{D}{Cr^2}\right)$$

and

$$\beta = \frac{9Kr^3}{\left(2\frac{\alpha e^2}{r} + 12.13.\frac{B}{r^{12}} - 6.7.\frac{C_3}{r^6}\right)} \qquad \ldots (4)$$

where

$$C_3 = C\left(1 + \frac{72}{42}\frac{D}{Cr^3}\right).$$

Following Mayer (1933), Mayer and Levy (1933) and Bleick (1934), optical data could be utilised to estimate the values of C and D, from which using the experimental values for the interaction distance, we can easily evaluate C_1, C_2 and C_3. The values of these constants for metal halides are given in Table I. The repulsive force parameter B, is given in Table II and is computed from equation (3) using the experimental values of β, T etc. as listed by Mayer *et al.*, (1933, 1934). From the knowledge of B and of C_1, C_2 and C_3, the lattice energies and the compressibilities for various salts can be calculated using equations (1) and (4). They are tabulated in Table III and IV respectively. In these

Tables, for the sake of comparison we have also reported values of E and β obtained by considering only the dipole dipole term.

TABLE I

Contribution of dipole-quadrupole term to lattice energy and compressibility

Crystal	$C \times 10^{60}$ (ergs $\times$ cm^6)	$C_1 \times 10^{60}$ (ergs $\times$ cm^6)	$C_2 \times 10^{60}$ (ergs $\times$ cm^6)
TlCl	2270	2601.0	2837.0
TlBr	2785	3192.0	3483.0
TlI	3930	4524.0	4943.0
AgF	305	357.2	394.8
AgCl	767	360.2	399.6
AgBr	967	358.3	396.8
AgI	850	1035.0	1168.0
CuCl	146	173.5	193.1
CuBr	198	234.5	260.4
CuI	330	391.0	434.9
NH_4F	217	251.8	276.7
NH_4Cl	1251	1421.0	1543.0
NH_4Br	1597	1814.0	1969.0
NH_4I	2286	2595.0	2816.0

TABLE II

Calculation of Repulsive Force Parameter B

Crystal	$B \times 10^{104}$ (with C term)	$B \times 10^{104}$ (with D term) Equ. 3
TlCl	318.4000	347.9000
TlBr	462.1000	507.0000
TlI	840.9000	955.7000
AgF	9.4990	10.2800
AgCl	39.7500	44.1400
AgBr	60.5300	66.9400
AgI	45.1500	51.3500
CuCl	4.6120	4.8990
CuBr	8.1060	8.6282
CuI	16.7000	18.0300
NH_4F	20.0700	20.9700
NH_4Cl	265.3000	280.7000
NH_4Br	449.9000	478.2000
NH_4I	1018.0000	1081.0000

energy form. The assumptions of a greater van der Waals potential, particularly for the case of iodide (say, for silver and copper) will result in a better agreement with the experiment.

The calculated compressibilities as given in Table IV, need to be multiplied by a correction term $F_{T,P}$ where

$$F_{T,P} = 1 + \frac{T}{\beta}(\partial\beta/\partial T)_P + \frac{T}{\beta^2 V}(\partial V/\partial T)_P(\partial\beta/\partial P)_T + \frac{2T}{3V}(\partial V/\partial T)_P$$

The experimental data for the terms appearing in this expression is not available in all cases and they can only be estimated in an indirect way. Therefore, this correction was not applied. However, the reported values of β are expected to change by about 7-8% on this account, as was seen by calculating this term for a few cases for which data were available. Keeping in mind, the effect of this correction, we can term the agreement between the theoretical and experimental values as satisfactory, except for thallium and ammonium salts, where the deviation are little more and cannot be accounted for successfully, due to uncertainty in experimental values.

The preceding treatment of the properties of metal halides shows that the Lennard-Jones (12 : 6) potential is quite adequate and practically equally successful for describing them as it is for molecular crystals and gaseous properties.

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